

CLAIMS

1. A proton conducting polymer membrane having a product ((S·day)/ $\mu\text{mol}$ ) of a proton conductivity (S/cm) at 23°C and a methanol barrier coefficient ((cm·day)/ $\mu\text{mol}$ ) at 25°C in an aqueous methanol solution of a specified concentration that satisfies at least one of either (A) or (B) below, wherein (A) the product in an aqueous methanol solution of 10% by weight is  $2.5 \times 10^{-4}$  (S·day)/ $\mu\text{mol}$  or more, or (B) the product in an aqueous methanol solution of 64% by weight is  $4.5 \times 10^{-5}$  (S·day)/ $\mu\text{mol}$  or more.
2. A proton conducting polymer membrane having an ion exchange capacity of 0.3 milli-equivalent/g or more, and having a crystalline phase.
3. The proton conducting polymer membrane according to claim 1 or 2, wherein the proton conducting polymer membrane comprises sulfonic acid groups.
4. The proton conducting polymer membrane according to any one of claims 1 to 3, wherein the proton conducting polymer membrane comprises a hydrocarbon polymer.
5. The proton conducting polymer membrane according to claim 4, wherein the hydrocarbon polymer comprises a crystalline aromatic polymer.

6. The proton conducting polymer membrane according to claim 5, wherein the crystalline aromatic polymer is polyphenylene sulfide.
7. The proton conducting polymer membrane according to any one of claims 1 to 6, wherein the proton conducting polymer membrane has an elongation at break of 10% or more as determined according to JIS K 7127.
8. The proton conducting polymer membrane according to any one of claims 1 to 7, wherein the proton conducting polymer membrane has a proton conductivity of  $1.0 \times 10^{-3}$  S/cm or more at 23°C.
9. The proton conducting polymer membrane according to claim 8, wherein the proton conducting polymer membrane has a proton conductivity of  $1.0 \times 10^{-2}$  S/cm or more at 23°C.
10. The proton conducting polymer membrane according to any one of claims 1 to 9, wherein the proton conducting polymer membrane has a methanol barrier coefficient of  $3.0 \times 10^{-4}$  (cm·day)/ $\mu\text{mol}$  or more at 25°C in an aqueous methanol solution of 64% by weight.
11. The proton conducting polymer membrane according to any one of claims 1 to 10, wherein the proton conducting polymer

membrane is irradiated with at least one radiation selected from the group consisting of  $\gamma$ -ray, electron beam and ion beam.

12. The proton conducting polymer membrane according to claim 11, wherein the dose of the radiation is from 10 kGy to 1,000 kGy.

13. A membrane-electrode assembly using the proton conducting polymer membrane according to any one of claims 1 to 12.

14. The membrane-electrode assembly according to claim 13, wherein at least one catalyst layer of the membrane-electrode assembly comprises a platinum and ruthenium catalyst.

15. A polymer electrolyte fuel cell using the proton conducting polymer membrane according to any one of claims 1 to 12, or the membrane-electrode assembly according to claim 13 or 14.

16. A direct methanol fuel cell using the proton conducting polymer membrane according to any one of claims 1 to 12, or the membrane-electrode assembly according to claim 13 or 14.

17. A method for manufacturing a proton conducting polymer membrane having a product ((S·day)/ $\mu$ mol) of a proton conductivity (S/cm) at 23°C and a methanol barrier coefficient

((cm·day)/ $\mu$ mol) at 25°C in an aqueous methanol solution of a specified concentration that satisfies at least one of either

(A) or (B) below, wherein

(A) the product in an aqueous methanol solution of 10% by weight is  $2.5 \times 10^{-4}$  (S·day)/ $\mu$ mol or more, or

(B) the product in an aqueous methanol solution of 64% by weight is  $4.5 \times 10^{-5}$  (S·day)/ $\mu$ mol or more,

the method comprising bringing a film comprising a hydrocarbon polymer into contact with a sulfonating agent.

18. A method for manufacturing a proton conducting polymer membrane having an ion exchange capacity of 0.3 milli-equivalent/g or more, and having a crystalline phase, the method comprising bringing a film comprising a crystalline hydrocarbon polymer into contact with a sulfonating agent.

19. The method for manufacturing a proton conducting polymer membrane according to claim 17, wherein the hydrocarbon polymer is a crystalline hydrocarbon polymer.

20. The method for manufacturing a proton conducting polymer membrane according to any one of claims 17 to 19, wherein the hydrocarbon polymer is polyphenylene sulfide.

21. The method for manufacturing a proton conducting polymer membrane according to any one of claims 17 to 20, wherein the sulfonating agent is at least one selected from the group

consisting of chlorosulfonic acid, oleum, sulfur trioxide and concentrated sulfuric acid.

22. The method for manufacturing a proton conducting polymer membrane according to any one of claims 17 to 21, wherein the film is brought into contact with the sulfonating agent in the presence of a solvent.

23. The method for manufacturing a proton conducting polymer membrane according to claim 22, wherein the solvent is a halide with three or more carbon atoms.

24. The method for manufacturing a proton conducting polymer membrane according to claim 22 or 23, wherein the solvent is at least one selected from the group consisting of 1-chloropropane, 1-bromopropane, 1-chlorobutane, 2-chlorobutane, 1-chloro-2-methylpropane, 1-bromobutane, 2-bromobutane, 1-bromo-2-methylpropane, 1-chloropentane, 1-bromopentane, 1-chlorohexane, 1-bromohexane, chlorocyclohexane and bromocyclohexane.

25. The method for manufacturing a proton conducting polymer membrane according to any one of claims 22 to 24, wherein the solvent is 1-chlorobutane.

26. The method for manufacturing a proton conducting polymer membrane according to any one of claims 17 to 21, wherein the

sulfonating agent is sulfur trioxide, and the film comprising the hydrocarbon polymer is brought into contact with a gas containing sulfur trioxide.

27. The method for manufacturing a proton conducting polymer membrane according to any one of claims 17 to 26, wherein the proton conducting polymer membrane is irradiated with at least one radiation selected from the group consisting of  $\gamma$ -ray, electron beam and ion beam.

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28. The method for manufacturing a proton conducting polymer membrane according to claim 27, wherein the dose of the radiation is from 10 kGy to 1,000 kGy.